

Complexes of Nickel(II) with Optically Active Diamines

By B. BOSNICH, J. H. DUNLOP, and R. D. GILLARD

[*Department of Chemistry, University College, London (B.B.); Department of Chemistry, The University, Sheffield (J.D.H. and R.D.G.)*]

THE electronic transitions which can be attributed to excitations between *d*-electron states in square planar diamagnetic *d*⁸ complexes have been the

subject of considerable attention, and various energy schemes have been suggested.¹ One useful method of obtaining such information is by the

¹ H. B. Gray, *Abstracts of the 8th Internat. Conf. on Co-ord. Chem.*, Vienna, 1964, 133 and references therein.

magnetic-dipole selection rules² in optically active complexes. Thus, if a transition is formally magnetic-dipole allowed in the microsymmetry of the complex, the asymmetry factor, g , should be ≥ 0.01 in the optically active complex and < 0.01 if the transition is magnetic-dipole forbidden. This rule is obeyed by the few optically active nickel complexes that have been studied; for example, g is 0.4 for ${}^3T_{2g} \leftarrow {}^3A_{2g}$ transition in α -nickel sulphate hexahydrate,³ and we have found that this same band, in the stereospecifically induced⁴ ion $D-[Ni(+)-pn_3]^{2+}$, ($pn = 1,2$ -diaminopropane), has $g = 0.23$ whereas the other two spin-allowed bands [${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$, ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$] have g factors < 0.01 (Table).

Complexes containing two molecules of diamine co-ordinated to nickel(II) may exist in either blue (octahedral, paramagnetic) or yellow (square planar, diamagnetic) forms. The most notable cases are the "Lifschitz salts"⁵ containing optically active stilbenediamine (stien). However, by varying the solvent used, it is possible to obtain either blue or yellow solutions of complexes of other diamines, such as 1,2-diaminopropane. The electronic spectra of such blue and yellow solutions are extremely similar to those of the analogous Lifschitz salts^{6,7} (Table). There seems no doubt that the electronic structure of the nickel ion is comparable in all blue bisdiamine complexes, and also in all yellow bisdiamine complexes.

complex and the distortion from cubic symmetry is small compared to the band width. The yellow diamagnetic square planar complexes of either amine show pronounced circular dichroism under the first visible absorption band at $445 m\mu$.

In general, diamagnetic square planar (D_{4h}) nickel(II) complexes have three spin-allowed $d-d$ transitions (${}^1E_g \leftarrow {}^1A_{1g}$, ${}^1A_{2g} \leftarrow {}^1A_{1g}$, ${}^1B_{1g} \leftarrow {}^1A_{1g}$) of which only the first two are magnetic-dipole allowed and thus, in optically active environments, should have $g \geq 0.01$. It is noteworthy that the circular dichroism band centred around $460 m\mu$ is displaced to the long-wavelength side of the absorption band (at $445 m\mu$). At $460 m\mu$ and longer wavelengths, g is 0.01, whereas at wavelengths below $445 m\mu$, g rapidly decreases. This is consistent with the postulate that this band contains at least two components.

In the system *trans*-[Co(+)- pn_2 Cl₂]Cl the well-separated magnetic-dipole allowed transitions, ${}^1E_g \leftarrow {}^1A_{1g}$ and ${}^1A_{2g} \leftarrow {}^1A_{1g}$, are respectively strongly negative and weakly positive in sign.⁸ If we assume that the same signs will be observed in the corresponding transitions in square planar nickel(II) complexes, it is likely that the negative circular dichroism band displaced to long wavelength ($g = 0.01$) is the ${}^1E_g \leftarrow {}^1A_{1g}$ component and the short-wavelength band ($g < 0.01$) is possibly the ${}^1A_{2g} \leftarrow {}^1A_{1g}$ component in the ion $[Ni(+)-pn_2]^{2+}$. That this latter component

TABLE

Complex	Solvent	Colour	λ	ϵ	g	λ	ϵ	g	λ	ϵ	g
$[Ni(+)-pn_3]^{2+}$	Acetone	blue	990	8	0.23	550	8	0.005	350	15	0.01
$[Ni(+)-pn_2]^{2+}$	H ₂ O/C ₂ H ₅ OH	blue	958	6.2	—	580	5	0.003	360	10.8	—
$[Ni(+)-pn_2]^{2+}$	CH ₃ NO ₂	yellow	445	15.5	0.01 ^a						

The absorption spectra^{6,7} and the circular dichroism for blue and yellow $[Ni(-)-stien_2]^{2+}$ are exactly parallel.

^a The maximum value at $460 m\mu$ where $\epsilon_t - \epsilon_r = -0.15$.

As expected, the blue and yellow forms of both $[Ni(+)-pn_2]^{2+}$ and $[Ni(-)-stien_2]^{2+}$ show Cotton effects in the $d-d$ band region, since the electronic transitions in all cases occur under the influence of the asymmetric field produced by the ligands. The blue paramagnetic complexes obey the magnetic-dipole selection rules for an octahedral

does not become positive may be due to the fact that there is considerable overlap in the absorption manifold. If our assignment is correct, the degenerate d_{xz} , d_{yz} orbitals lie above the d_{xy} orbital in these nickel complexes.

(Received, March 24th, 1965.)

² S. F. Mason, *Proc. Chem. Soc.*, 1962, 137.

³ V. Rudnick and L. R. Ingersoll, *J. Opt. Soc. Amer.*, 1942, **32**, 622.

⁴ E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 2620.

⁵ I. Lifschitz, J. G. Bos, and K. M. Dijkema, *Z. anorg. Chem.*, 1939, **242**, 97.

⁶ C. Furlani and G. Satori, *J. Inorg. Nuclear Chem.*, 1958, **8**, 126.

⁷ W. C. E. Higginson, S. C. Nyburg, and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 468.

⁸ R. A. D. Wentworth and T. S. Piper, *ibid.*, 1965, **4**, 202.